



Conversion of slaughterhouse and poultry farm animal fats and wastes to biodiesel: Parametric sensitivity and fuel quality assessment



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ABSTRACT

Over recent past, animal fat wastes have drawn significant attention for the production of biodiesel all around the globe. The present article provides a comprehensive review on the production of biodiesel from various slaughterhouse animal fats (SHAFs) waste resources viz. beef tallow, pork lard, mutton fat, lamb meat, fleshing oil as well as poultry fats (PFs) and wastes viz. chicken fat, duck tallow and feather meal. Methods of physical-pretreatment of SHAFs and PFs for recovering usable fat and subsequent chemical pre-treatment for reduction of free fatty acids have been enumerated. Biodiesel synthesis processes through both single and two-step trans/esterification employing homogeneous and heterogeneous catalytic routes have been critically assessed. Advantages of reusability of heterogeneous catalysts over their homogeneous counterparts have been elucidated. Besides, parametric effects viz. catalyst concentration, temperature, pressure and alcohol to fat ratios on biodiesel yield along with optimal process conditions have been meticulously presented. Relative merits and demerits of enzymatic and supercritical conversion processes have been highlighted. Current advancements in process intensification technologies have been assessed and comparative appraisals of biodiesel properties produced from various SHAFs and PFs have also been decisively summarized.

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Abbreviations: SHAF, slaughterhouse animal fat viz. BT beef tallow; PL, pork lard; FO, fleshing oil; LM, lamb meat; MF, mutton fat; PFs viz. CF, poultry fats viz. chicken fat; DT, duck tallow; FM, feather meal; MR, molar ratio; HAC, homogeneous acid catalyzed; HBC, homogeneous base catalyzed

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1. Introduction

1.1. Selection of biodiesel feedstock

In this modern era, increasing dependence upon fossil-diesel fuel in automobiles and other industries has essentially led to search for alternative sources of energy to replace or supplement depleting petro-fuels from the earth crust [1]. The energy demand of the world will prospectively increase by almost 50% in 2030 and it is important to note that India and China would account for 45% of its usage. Thus, biodiesel could be a very suitable option to cut emissions, to support transportation sector relying heavily on diesel fuels and to maintain an environmentally benign atmosphere. The primary advantage of using biodiesel lies in its biodegradability, renewability and ease of combustion. Reduction of CO₂ emissions and promotion of rural economic development are other bright aspects of using biodiesel as a substitute fuel measure [2]. There are host of feedstocks for biodiesel production; however, judicious selection of feedstock should involve consideration of two vital factors i.e. low cost of production and production in bulk scale; and thus, selecting the cheapest source is crucial for minimizing production cost [3]. The major feedstocks for biodiesel production can be subdivided into following categories as follows [4–18]:

1. Edible vegetable oil: sunflower, soybean, rapeseed, palm, canola, coconut, peanut, mustard and rice bran oil.
2. Non-edible vegetable oil: jatropha, microalgae, safflower oil and linseed oil.
3. Waste recycled oil: waste frying oil and waste acidified oil.
4. Animal fats: (a) slaughterhouse animal fat (SHAF) viz. beef tallow (BT), pork lard (PL), fleshing oil (FO), lamb meat (LM), mutton fat (MF); and (b) poultry farm animal fats/poultry fats (PFs) viz. chicken fat (CF), duck tallow (DT) and feather meal (FM).

Biodiesel, prepared from animal fat-more specifically SHAFs and PFs, is popularly known as 'second generation biodiesel' and has the potential to meet the global energy needs owing to overall cost-effectiveness and acceptable fuel properties.

1.2. High FFA feedstocks: SHAF and PF vs. waste frying oil

Though waste frying oil (WFO), SHAFs and PFs all are FFA rich cost-effective resources, the supply chains of SHAFs and PFs are more centralized than those of WFO due to the availability of WFO only from household kitchen and local restaurants. Moreover, the availability of inedible fat from slaughterhouses and poultry farms is in abundance as compared to that of WFO. Kumar et al. [19] pointed out that animal fat could not be directly incorporated into diesel engines due to its high viscosity. Therefore, efficient technology like

trans/esterification could be highly beneficial for fuel property improvement and emission reduction of diesel engines. It was also highlighted that SHAF production in Europe is pretty high making it more attractive to be used as promising feedstock for production of diesel fuel. A detailed comparison revealed that the properties of SHAF biodiesel matched very closely to that of diesel [20]. It was reported that annually, around 2.5 billion pounds of waste restaurant lipids were obtained in form of SHAFs and PFs from restaurants and fast food centers in US [21] with potential for conversion into biodiesel. Nelson and Schrock [22] reported an informative cost analysis illustrating that for a fixed plant capacity, the cost of biodiesel production was highly sensitive to beef tallow (BT) price. Notably, the resource availability analysis predicted that about 4 billion pounds of edible and inedible BT were being produced in slaughterhouses of 11 states of US that could lead to production of 551 million gallons of biodiesel.

Thus, it is apparent that, different SHAFs and PFs e.g. BT, PL, CF, DT, FO, MF, LM, and FM can be very potential source for biodiesel production owing to sustainable availability due to better supply chain and economic feasibility. The present paper primarily attempts to overview the methods of extraction of useable fat from SHAFs and PFs and its subsequent conversion to biodiesel through catalytic, enzymatic and supercritical methods. The parametric effects on biodiesel yield have been critically assessed for both one step and two-step processes. The fuel properties of the product biodiesel derived from various SHAFs and PFs have been comprehensively underlined. Besides, recent advancements in process intensification in biodiesel synthesis have been meticulously presented. This article, thus, aims at providing valuable information to researchers through a comprehensive overview of biodiesel production from low cost-SHAF and PF feedstocks towards further advancement for sustainable development in this promising arena.

1.3. Qualitative analyses of SHAFs and PFs

It [23] was emphasized that usage of low quality feedstocks containing high FFA's and water could cause serious technical difficulties in biodiesel production. Fatty acid profiles of SHAFs viz. PL, BT, FO and PFs viz. CF, mixed fat, DT are presented in Tables 1 and 2 respectively. It is important to note that energy content of biodiesel is a function of energy content of its corresponding feedstock and greater unsaturation in biodiesel leads to a lower heating value [24]. Greater acid number (AN) [25] of SHAF or PF suggests that direct transesterification could lead to formation of soaps; thus, a pre-treatment including esterification with alcohol could reduce the FFA content of the feedstock. Higher value of iodine number in SHAF or PF sample signifies greater level of unsaturation. Kinematic viscosity is another vital property of a feedstock that is a measure of resistance offered to flow and shear [26]. The properties such as acid number, iodine number, kinematic viscosity and higher heating values of SHAFs viz. PL, BT and FO were evaluated and summarized in Table 3.

Table 1
Fatty acid profiles of different SHAF feedstocks.

Fatty acids	Pork lard [85] (wt%)	Beef tallow [24] (wt%)	Fleshing oil [29] (wt%)
Palmitoleic (C16:1)	2.2	1.90	5.10
Palmitic (C16:0)	23.7	26.18	27.25
Stearic (C18:0)	12.9	33.69	13.23
Oleic (C18:1)	41.4	30.09	42.06
Linoleic (C18:2)	15.0	0.76	2.04
Linolenic (C18:3)	1.0	–	0.16
Myristic (C14:0)	1.3	2.68	3.18
Myristoleic (C14:1)	–	–	1.27
Margaric (C17:0)	–	–	0.94
Heptadecenoic (C17:1)	0.4	1.74	–
Arachidic (C20:0)	0.2	0.30	0.21
Eicosenoic (C20:1)	0.9	–	–
Eicosadienoic (C20:2)	0.7	–	–
Eicosatrienoic (C20:3)	0.2	–	–
Saturated fatty acids	–	65.52	–
Unsaturated fatty acids	–	34.48	–

Table 2
Fatty acid profiles of different PF feedstocks.

Fatty acids	Chicken fat [112] (wt%)	Mixed fat [98] (wt%)	Duck tallow [91] (wt%)	Poultry fat [92] (%m/m)
Palmitoleic (C16:1)	7.7	3.4	–	3.62
Palmitic (C16:0)	21.0	26.6	17.0	25.57
Stearic (C18:0)	5.5	16.7	4.0	7.75
Oleic (18:1)	48.5	42.1	59.4	36.64
Linoleic (18:2)	17.3	7.6	19.6	24.69
Linolenic (18:3)	0.0	0.57	–	1.02
Myristic (C14:0)	–	2.1	–	0.70
Myristoleic (C14:1)	–	–	–	–
Margaric (17:0)	–	–	–	–
Heptadecenoic (C17:1)	–	–	–	–
Arachidic (C20:0)	–	–	–	–
Eicosenoic (C20:1)	–	–	–	–
Eicosadienoic (C20:2)	–	–	–	–
Eicosatrienoic (C20:3)	–	–	–	–
Saturated fatty acids	–	–	–	34.03
Unsaturated fatty acids	73.5	–	–	65.98

Table 3
Characteristics of SHAF feedstocks viz. pork lard, beef tallow and fleshing oil.

Parameter	Pork lard [31]	Beef tallow [31]	Fleshing oil [29]
Acid number (mg KOH/g of fat)	0.63	1.07	24.30
Iodine number (g/100 g of fat)	77.9	46.37	75
Kinematic viscosity at 40 °C (mm ² /s)	39.53	46.37	43.33
Higher heating value (MJ/kg of fat)	39.5	38.9	39.572

1.4. Physical pre-treatment of SHAFs and PFs

Physical pre-treatment of SHAF and PF prior to trans/esterification includes removal of moisture and suspended impurities and

extraction process to recover useful fat as feedstock for biodiesel synthesis. Different methods were adopted to extract useable fat from SHAF among which melting and supercritical CO₂ extraction had been usually used; the methods are meticulously reviewed in the following sections.

1.4.1. Extraction of fat from SHAF and PF by melting

Primarily, extraction of usable fat from SHAF was performed by simple melting at around 100–110 °C. Pork wastes [27] were extracted by melting, followed by separation of solid residue. Same procedure as above was reported to remove water and insoluble matter from CF [28]. FO used for biodiesel synthesis is itself a melted product of fleshing wastes [29]. Beef and CF were slowly heated at 100 °C under reduced pressure to melt the fat for simultaneous removal of suspended and residual matter [30]. Slaughterhouse CF and MF were extracted by melting at 60 °C under reduced pressure for separation of waxy and suspended colloidal matter [17]. About 70% of the moisture was simultaneously removed while melting at 110 °C for the extraction of PL, CF and BT from the corresponding SHAF and PF followed by percolation and filtration operation for removal of suspended matter and obtaining useful fat [31]. Slaughterhouse CF was dried at 110 °C temperature to make it dry for its direct usage in transesterification reaction [32]. In an attempt to extract fat from FM [33], 100 g of FM sample was stirred with 300 mL of water at 70 °C for 20 min followed by melting of adsorbed fat on the protein part of FM and recovered as top layer. Subsequently, the top layer underwent decantation and centrifugation rigorously under 5000 rpm for 10 min for collection of the fat from FM. Thus, it may be concluded that animal fat were heated at different temperatures for the extraction of the worthwhile fat material through removal of suspended impurities. In another work by Bharat and Bhattacharya [34], slaughterhouse pork skin and chicken skin fat were extracted by employing a high pressure cooking mechanism to obtain useful fat.

1.4.2. Extraction of fat from SHAF by supercritical CO₂ (SC-CO₂)

Taher et al. [35] reported the usage of continuous extraction of fat from LM by SC-CO₂ extraction proving it to be a very effective chemical solvent extraction process. The optimum conditions were determined as 45 °C, 500 bar and 3 mL min^{−1} CO₂ flow rate at which, 87.4% of total fat content was extracted from freeze-dried meat. Zuhair et al. [36] demonstrated parametric effects viz. drying technique, meat source, grinding, SC-CO₂ flow rate, extraction pressure and extraction temperature on fat extraction yield from LM. A linear decrease in extraction yield and efficiency on increasing the SC-CO₂ flow rate from 3 to 5 mL min^{−1} was observed. Increase in pressure from 300 to 500 bar at 55 °C temperature could result enhanced fat yield; while, on the other hand the extraction efficiency and yield increased from 35 to 45 °C but eventually diminished on further increase in temperature up to 55 °C.

1.5. Homogeneous and heterogeneous catalytic conversion of SHAF and PF

The application of a suitable catalyst plays a pivotal role in converting feedstocks to biodiesel through trans/esterification. The usage of homogeneous base catalysts viz. NaOH and KOH can produce quality biodiesel from feedstocks having lower FFA content [37,38]. Feedstocks containing high quantity of FFA render it to react with the base catalyst resulting in formation of soaps [39]. On the other hand, use of homogeneous acid catalysts prevents the formation of soaps but the rate of transesterification with acid catalysts could be 4000 times slower than its base

counterpart [37]. Superior technical practicability and lower system complexity are the key advantages of homogeneous acid catalyzed process over its base equivalent [40]. In spite of the fact that, fixed capital cost of homogeneous base catalyzed process was less, nevertheless, cost estimation analysis has proven that acid catalyzed protocol being a single step trans/esterification process may prove to be much more cost effective in terms of gross manufacturing cost, lower break-even price and rate of tax return [41].

A very informative and critical review has been accomplished emphasizing on the usage of base heterogeneous catalysts for biodiesel production [42]. Borges and Díaz [43] underlined and elucidated three different processes viz. transesterification, esterification and two step esterification–transesterification involving novel heterogeneous catalysts for biodiesel production. Related work [44] enumerated transesterification of lower FFA feedstocks using SrO and CaO base catalysts which rendered a conversion of > 95%. However, ability to catalyze simultaneous esterification and transesterification of high acid number (AN) feedstocks offers the usage of heterogeneous acid catalyst an upper edge over its base counterpart [45]. Amorphous zirconia catalyst was used for the transesterification of high FFA feedstock and about 95% yield was obtained [46]. Tungsten oxide–zirconia was employed as a super solid acid catalyst for the transesterification of high FFA feedstock having 54.9% of FFA and consequently a high biodiesel yield of 96% could be achieved [47]. Solid acid catalysts when employed for the transesterification of a variety of low FFA feedstocks rendered an appreciable yield [48–55].

1.6. Emission issues and fuel quality evaluation

Many works addressing acceptability of biodiesel in terms of emission issues and fuel properties had come up [56–60]. Although use of biodiesel and its blends increases NO_x emissions, but this rising effect can be mitigated by employing engine and fuel modifications through various techniques [61]. Apart from these, many works [62–67] revealed a promising picture of the growing need for biodiesel. Infrared techniques were investigated as rapid, low cost and reproducible analyzing tools for both qualitative and quantitative analysis of biodiesel and have a very high prospect in analysis of biodiesel [68]. Technical aspects including parametric sensitivity, operating conditions, analytical tools for monitoring transesterification reaction and the fuel properties had been assessed [69–70].

2. Two-step process for conversion of SHAFs and PFs to biodiesel

Two-step process usually consists of upstream acid esterification of FFAs followed by downstream base catalyzed transesterification of triglyceride.

2.1. Upstream esterification of physically pre-treated SHAF and PF

SHAF usually contains a very high proportion of FFAs i.e. high AN [71]. FFA and Water content are two limiting factors that affect the production of biodiesel from SHAF. To overcome these problems, pre-esterification of SHAF, PF and their wastes were performed by employing methanol/ethanol in presence of acid homogeneous catalyst, among which H_2SO_4 exhibited very promising results. The AN for the waste lard [27] was quite high ($14.57 \text{ mg KOH g}^{-1}$) which needed to be reduced to 1 mg KOH/g of fat (to avoid soap formation) and the water content should be below 0.3% for convenient production of biodiesel through

subsequent base catalyzed process [72]. Thus, it was emphasized that reduction of FFAs is a must through the pre-esterification process prior to downstream transesterification [73,74]. Likewise, Pereira et al. [75] synthesized biodiesel from BT using the pre-esterification technique employing sulfuric acid as acid catalyst using ethanol.

The parametric effects of catalyst quantity in reducing the FFA content of waste PL was studied [27]. An increase in H_2SO_4 concentration from 1 to 3 wt% resulted in enhancement in biodiesel purity up to 96.5%; however, further increase led to decrease in purity to 90% ascribing to augmented mass transfer limitations due to increased density of reaction mass at higher catalyst concentration. Canakci and Gerpen [76] investigated two-step H_2SO_4 pre-treatment of a simulated animal fat (prepared by adding 20 wt % and 40 wt% palmitic acid to soybean oil) with high FFA content. In the first step, the AN could be reduced to $2.87 \text{ mg KOH g}^{-1}$ followed by reduction to less than 2 mg KOH/g in the second step making it a very effective process of reducing FFA content. However, there was a significant reduction in the AN to $1.37 \text{ mg KOH g}^{-1}$ fat on increasing the H_2SO_4 concentration up to 15% under methanol to fat molar ratio of 10:1 in 30 min reaction time. Moreover, it was also revealed that ethanol could reduce the FFA level of the synthetic fat faster than methanol. In another effort to synthesize biodiesel from FO (AN of 24.30 mg KOH/g) obtainable from leather industry, Alptekin et al. [29] conducted the pre-esterification of FO by using H_2SO_4 with reaction temperature and duration of 60°C and 1 h respectively. Sulfuric acid quantity ranging from 1%, to 15% was used at constant reaction temperature of 60°C for 1 h. Consequently, it was observed that 1% H_2SO_4 merely reduced AN to just 22.12 mg KOH/g ; notably, on increasing H_2SO_4 concentration to 15%, the AN decreased remarkably to $1.43 \text{ mg KOH g}^{-1}$. Encinar et al. [71] used waste inedible fats (WIF) having high AN ($21.2 \text{ mg KOH g}^{-1}$), to produce biodiesel and conducted pre-esterification of the feedstock with H_2SO_4 , H_3PO_4 and p-TsOH under different reaction conditions. It was observed that increasing methanol to WIF ratio led to lower final AN; however, inherently associated with increased total costs of biodiesel production. Although, H_2SO_4 and p-TsOH were proved effective in lowering the AN of the fat giving maximum ester content of 98.9%, however, employment of H_3PO_4 displayed disappointing results due to soap formation. Gürü et al. [28] synthesized biodiesel from waste CF through two-step catalytic process comprising of an optimized pre-esterification step under 0.20 (w/w) methanol/CF ratio, 0.08 (w/w) H_2SO_4 /CF ratio at 40°C for 30 min prior to trans-esterification. On the contrary, Alptekin and Canakci [32] conducted pre-treatment of CF using a much higher H_2SO_4 concentration (20 wt%) and methanol to CF molar ratio of 40:1 for 80 min at 60°C for obtaining a final FFA content of only 0.67%. The product FAME mixture was separated from alcohol–water through decantation and subsequent heating at 110°C before subjecting it to the downstream transesterification.

In this context, it should be noted that, during the esterification reaction there is inevitable occurrence of simultaneous transesterification reaction, both lead to the production of biodiesel; however, extent of transesterification is significantly less in comparison with that of esterification; thus, the upstream pre-treatment is usually referred to as esterification only.

2.2. Downstream transesterification

Gürü et al. [28] elucidated the parametric effects of temperature, molar ratio of methanol to pre-esterified CF and weight ratio of NaOH to pre-esterified CF on biodiesel yield in the downstream step of a two-step conversion process. Temperature displayed synergetic effect on biodiesel yield up to 62°C ; however, further

increase led to slow depreciation in yield thereafter. Similarly, an increase in methanol to CF ratio from 0.25 to 0.35 led to maximization in biodiesel yield; nevertheless, further increment of molar ratio up to 0.40 exhibited insignificant enhancement in product yield. NaOH to CF weight ratio was found to enhance yield steadily, nonetheless, above 0.010 there was a declining trend in biodiesel yield possibly owing to incremented formation of sodium salts of fatty acids. Notably, Alptekin and Canakci [32] used four different alkaline catalysts viz. NaOH, KOH, sodium methoxide and potassium methoxide for the transesterification of CF after reducing the FFA level of the CF below 1%. Consequently, it was lucidly revealed that FAME yield could be enhanced appreciably to 88.5% by increasing the reaction temperature from 25 to 60 °C; however, reaction time and KOH concentration had insignificant effects on FAME yield. Downstream transesterification of upstream pre-esterified WIF [71] was done by employing 1 wt% KOH and a maximum biodiesel purity of 97.3% was obtained. On the contrary, a lower optimum yield of 89.0% was achieved at 6:1 M ratio of alcohol to WIF after 48 h of reaction under acid catalyzed transesterification process. Canakci and Gerpen [76] conducted alkaline transesterification of BT and CF utilizing different KOH concentration (0.75%, 1.00%, 1.25%, 1.75% weight of fat) and it was determined that 1.25 wt% KOH rendered optimum yield of 82.1% and 88.7% for BT and CF respectively. Notably, biodiesel yield decreased beyond 1.25% of KOH attributing to the formation of fatty acid soaps. In another work [77], pre-esterified PL and BT were transesterified by employing NaOH as homogeneous alkaline catalyst. The authors explored that a blend of BT methyl esters and PL methyl esters in 1:4 proportion could exhibit better fuel quality compared to individual methyl ester.

3. Single-step transesterification

Single-step transesterification of SHAFs and PFs is usually preceded by both physical and chemical pre-treatments as detailed in the following sections.

3.1. Physical pre-treatment

Physical pre-treatment of SHAF and PF involves removal of moisture, suspended impurities and extraction of the useful fat prior to transesterification as elaborated in Section 1.4.

3.2. Chemical pre-treatment

In an effort to reduce FFA content of feather meal, Kondamudi et al. [33] mixed the physically pre-treated SHAF i.e. melted and purified fat with KOH solution to remove the FFA in form of soaps followed by separation of soaps by centrifugation. In the work by Cunha et al. [78], mixture of CF and swine fat was washed with 600 ml of 1 M Na₂CO₃ aqueous solution under mechanical stirring for 10 min followed by centrifuging at 3000g (10 min, 15 °C). Thereafter, the supernatant was separated and dried with anhydrous sodium sulfate and the dried material was finally centrifuged rendering 60% recovery of treated fat from the initial PFs. Thus, alkaline treatment rendered loss of FFA from feedstock.

3.3. Homogeneous catalytic transesterification

3.3.1. Homogeneous base catalyzed (HBC) transesterification

The effects of important process parameters on the yield and purity of biodiesel produced from pre-treated SHAF and PF have been critically assessed in the following sections.

3.3.1.1. Catalyst. NaOH and KOH had been extensively employed as HBC by majority of researchers for transesterification of fat derived from variety of SHAFs and PFs. Catalyst concentration is an important factor in the transesterification of animal fat for the synthesis of biodiesel. Encinar et al. [71] demonstrated the effects of catalyst type and concentration on the FAME yield from BT employing both NaOH and NaMeO catalysts at different concentrations of 0.1, 0.3, 0.5, 0.7, 0.9 (w/w). The 0.3% NaOH and 0.5% of NaMeO gave the maximum yield of BT methyl ester; suggesting that NaOH is more effective base catalyst than NaMeO for the transesterification of BT. Taravus et al. [79] used 1 wt% NaOH for the transesterification of sunflower oil-BT blend at 1 atm, 60 °C. They concluded that for feedstock with higher than the threshold 40% BT content, product specifications deviated from the biodiesel standards of ASTM D 6751 and EN 1424. Whereas, KOH concentration of 1.5 wt% of pre-treated BT [80] at 65 °C and 6:1 M ratio of methanol to BT rendered a transesterification yield of 97% biodiesel. In an effort to perform continuous biodiesel production, a tubular reactor was operated (800 L/day) at 65 °C by employing KOH as HBC and approximately 95% conversion of pre-treated BT was achieved [81]. Biodiesel could also be produced from BT by employing 1 wt% of 90% pure NaOH (non-AR grade) and thin layer chromatography displayed minimal impurities in form of mono, di and triglycerides in final biodiesel demonstrating a high conversion to methyl esters [82].

Bhatti et al. [17] carried out the KOH catalyzed transesterification of CF and MF giving an optimum yield of 88.14 ± 1.12 and $78.33 \pm 1.23\%$ respectively which is less as compared to the yield obtained by single-step acid transesterification reaction; which may be attributed to the soap formation in KOH process. A blend of chicken-swine fat was transesterified with KOH as base catalyst and optimization with response surface methodology (RSM) showed a maximum conversion of 83.5% at catalyst concentration of 0.96 wt%. Notably, this low conversion of ethyl esters might probably be due to the negative impact of formation of soaps through reaction between FFAs and KOH [78].

Isler et al. [83] elucidated the effect of increasing alkali catalyst concentration on the yield of biodiesel from raw FO by considering four different levels of NaOH at 0.25, 0.50, 0.75 and 1 wt%. The results indicated that biodiesel yield increased on augmenting the catalyst concentration from 0.25 to 0.75 wt% and the yield remained the same even upon further increase in NaOH concentration; thus, 0.75 wt% NaOH was the optimum quantity giving approximately 100% yield after 20 min of reaction time. Biodiesel from FM was obtained using KOH and 1 wt% catalyst was optimum for the transesterification reaction [33]. Oner and Altun [84] carried out the NaOH catalyzed transesterification of the melted fat obtained from inedible tallow at 6:1 M ratio methanol/tallow, 60 °C for 3 h. The biodiesel was successfully tested in diesel engine as pure (B100) and as 5%, 20%, and 50% blend with diesel fuel by volume (B5, B20, and B50, respectively).

In the study of Dias et al. [85], NaOH catalyzed transesterifications of soybean oil-PL and waste frying oil-PL blend revealed that 0.8 lard weight fraction in above two blends provided a maximum yield of 88.6 and 88 wt% respectively. In contrary, it was witnessed that 100% lard in above two blends gave a lower yield of 81.7 wt% each and with increasing oil fraction led to increased yield of biodiesel. Thus, it was suggested that a proper mix of oil and PL could result acceptable physical characteristics of the resultant biodiesel. In an optimization study [86] using RSM, an average biodiesel yield of $97.8 \pm 0.6\%$ was achieved from pre-treated PL using an optimum KOH quantity of 1.26%. At a constant reaction temperature and time, increase in catalyst concentration from 0.6 to 1.2 wt% led to an increase in biodiesel yield; nevertheless, 0.9 wt% was determined as the optimum quantity. The maximum experimental FAME yield failed to fulfill EN 14214 standard

specifications [87]. In another effort to produce biodiesel from PL [88], among four different NaOH concentrations (0.40, 0.60, 0.80 and 1 wt%); 0.40 wt% provided the highest biodiesel yield. The result signified that merely increasing the catalyst quantity did not guarantee higher product yield and there is always an optimal catalyst concentration under the influence of other process parameters.

3.3.1.2. Temperature. Temperature is another important factor affecting the homogeneous base catalyzed transesterification of SHAFs and PFs. Biodiesel was obtained from BT by accomplishing transesterification at reaction temperature of 60 °C [79,89,31,30,82] and 65 °C [80,90]. Thus, the temperature range of 60–65 °C may be considered to be most usual to give acceptable yields of FAME and FAEE from BT. Hoque et al. [30] probed the effect of temperature on biodiesel yield at 55 °C, 60 °C and 65 °C for both BT and CF. They concluded that for every 5 °C rise in temperature, the yield of biodiesel increased while keeping other factors viz. methanol to oil molar ratio, catalyst concentration, reaction time and stirring speed constant and 65 °C was found as the optimum temperature giving an appreciable 87.4 and 89% yield for BT and CF biodiesel respectively. Cunha Jr. et al. [78] evaluated the temperature effects on the yield of biodiesel from mixture of CF and swine fat selecting 30 °C, 50 °C and 70 °C. It was observed that there was no proper phase separation at 70 °C on account of which it was rejected as the optimum temperature despite giving a considerably good yield of 96.2%. Accordingly, 30 °C was selected as the best condition although providing a much lower 83% conversion.

Isler et al. [83] demonstrated the effects of temperature on biodiesel yield from FO as function of time at five levels ranging from 40 °C to 60 °C. It was demonstrated that reaction at 40 °C took maximum time of 1 h while at 45 °C only half an hour of reaction time was required to achieve the same yield. Notably, on further increase in temperature to 50 °C, 55 °C and 60 °C, the reaction could be completed in just one third hour attaining cent per cent conversion. Thus, 50 °C was selected as the optimum temperature for the transesterification of FO.

Jeong et al. [86] carried out the transesterification of PL at five different temperature levels viz. 24.8 °C, 35 °C, 50 °C, 65 °C and 75.2 °C. The results exhibited a very interesting trend indicating that at lower alcohol to oil ratio, an increase in temperature could augment the FAME yield. However, 65 °C was the optimum temperature as higher reaction temperature led to methanol evaporation resulting in a significant reduction in biodiesel yield. Berrios et al. [87] employed a constant reaction temperature of 60 °C for all the experiments conducted for the transesterification of PL. While studying community scale biodiesel production from PL in Thailand, Phalakornkule et al. [88] conducted all the experiments at a constant temperature of 65 °C for single-step base catalyzed transesterification of PL.

In the work by Chung et al. [91], effect of temperature on biodiesel yield from DT were studied using four different temperature levels of 55 °C, 65 °C, 75 °C and 85 °C. It was a bit unexpected to observe that the yield remained constant throughout at 97%; this might be ascribed to attainment of equilibrium yield at lower temperature itself.

Thus, optimization studies on reaction temperature proved that on account of improper phase separation or other technical difficulties (viz. attainment of reaction equilibrium) at higher temperature, optimum yield of SHAF or PF biodiesel was always obtained at an optimum temperature for most biodiesel production processes involving homogeneous base catalysts.

3.3.1.3. Alcohol type and concentration. Commonly, both methanol and ethanol were used for the HBC transesterification of SHAFs

and PFs. Methanol was used in majority of works including the transesterification of SHAF viz. BT, FO, PL [30,31,79,80,83,86,89,90] and PF viz. CF, DT, FM [17,30,33,92,91]. Ethanol route of synthesis was also used for carrying out the transesterification reaction of SHAF viz. PL and BT [93] and PF viz. CF [78,92]. Though, the required stoichiometry shows 3:1 M ratio (MR) of alcohol to fat but a greater MR was desirable to shift the equilibrium towards the FAME side [94]. It was sighted that methanol to fat ratio of 6:1 was most preferred by the researchers for conversion of BT to biodiesel [30,31,79,80,82,89]. In the work by Hoque et al. [30], it was stimulating to note that biodiesel yield initially increased to 76 and 78% for BT and CF respectively on increasing the MR of methanol to fat from 3:1 to 6:1; however, decreased to 60 and 62% at 12:1 ratio. The authors inferred that reduction in the yield might be due to deactivation of the catalyst (KOH) by excess methanol and accordingly 6:1 ratio was selected as the optimum MR for the transesterification. Garcia et al. [93] carried out single-step methanolysis and ethanolysis of slaughterhouse pork and beef fat at alcohol to fat MR of 6:1 that resulted in biodiesel yield of 87.7 and 86.3% with methanol and 78.4 and 82.7% using ethanol respectively. It was noticeable that for the same MR, the yield of biodiesel achieved using methanol was greater than that gained by ethanol possibly due to greater miscibility of methanol with both feedstocks.

Kondamudi et al. [33] carried out the transesterification of FM using a higher (9:1) MR of methanol to FM, but only a small 7–11% biodiesel yield was obtained. While conducting transesterification of FO, Isler et al. [83] used four levels of methanol to FO ratio ranging from 3:1 to 6:1. The result indicated that reaction carried under MR of 5:1 was completed within 20 min and the one under 6:1 was completed just within 15 min and thus, 6:1 methanol to oil ratio was selected as the optimum MR giving cent per cent biodiesel yield.

Shin et al. [94] examined the effect of MR of methanol to refined lard on biodiesel purity and observed that on increasing ratio from 30:1 to 45:1, the yield increased in direct proportion but beyond 45:1 MR, the yield remained unchanged (possibly due to attainment of reaction equilibrium). Phalakornkule et al. [88] reported transesterification of PL at four levels of methanol to oil MR of 6:1, 7.5:1, 8.4:1 and 9:1 and it was revealed that 9:1 furnished the uppermost conversion to biodiesel.

Optimization studies were carried out according to 3³ factorial design to determine the optimum conditions for the transesterification of CF-swine fat blends at ethanol to fat MR of 6:1, 7:1 and 9:1; and 7:1 ratio was the optimum one giving 83.5% biodiesel yield under mild temperature of 30 °C [78]. While studying the effects of alcohol to DT ratio on biodiesel yield, Chung et al. [91] explained that on increasing the MR of methanol to DT from 3:1 to 6:1, there was a momentous increase in biodiesel yield from 75% to 97%; however, it again decreased linearly to 75% on increasing the ratio to 18:1; thus, establishing 6:1 as the optimum MR.

Thus, it may be concluded that optimization studies are essential to determine most appropriate MR of alcohol to fat; and mere increase in MR may not always guarantee higher conversions.

3.3.2. Homogeneous acid catalyzed (HAC) transesterification

The effects of main governing process factors on the homogeneous acid catalyzed transesterification of SHAFs and PFs have been elucidated in the following sections.

3.3.2.1. Catalyst. Soap production is the primary disadvantage of using base catalysts for the transesterification of SHAF having high FFA content. This limitation can be eliminated by using HACs. There has been a very meager work reported on HAC transesterification of SHAF.

2.25 M 10 wt% H_2SO_4 was used for obtaining methyl and ethyl esters from SHAF and a maximum mass conversion of 78% was reported [96]. Encinar et al. [71] reported H_2SO_4 catalyzed transesterification and found that 9% H_2SO_4 provided optimum 90% biodiesel yield. Likewise, Bhatti et al. [17] conducted transesterification of CF and MF using H_2SO_4 and reported that optimum H_2SO_4 concentration for CF and MF were 25 wt% and 50 wt% at 1:30 fat to methanol MR providing $99.01 \pm 0.71\%$ and $93.21 \pm 5.07\%$ biodiesel yield respectively, at the expense of long 24 h reaction time. Biodiesel yield from CF was always greater than that from MF under identical conditions. For both CF and MF, biodiesel yield could be enhanced with increase in H_2SO_4 concentration from 20 to 60 wt%, nevertheless, further increase in catalyst quantity resulted in reduction in the biodiesel yield possibly due to a mixing problem at higher catalyst concentration. Thus, it may be concluded that HAC transesterification requires greater concentration of catalyst compared to its base counterpart to achieve equivalent biodiesel yield.

3.3.2.2. Temperature. Temperature too plays a very vital role in acid HAC transesterification of SHAFs and PFs. Inadequate work had been reported on the effect of temperature on biodiesel yield. Bhatti et al. [17] studied H_2SO_4 catalyzed transesterification of CF and MF at four different temperatures viz. 30, 40, 50 and 60 °C. With a variation in temperature from 30 °C to 60 °C, CF rendered maximum biodiesel yield at a 50 °C temperature lower than that of MF which exhibited maximum yield at 60 °C. The reason behind such behavior was attributed to the presence of higher amount of FFA in MF. In another research [96], H_2SO_4 catalyzed conversion of SHAF into ethyl and methyl biodiesel was investigated at 50 °C, 70 °C and 90 °C. Prominent interaction between time and temperature was observed for all conversions and it was revealed that on increasing reaction temperature (at the expense of increased cost of energy), the reaction time could be reduced. Accordingly, 50 °C was considered as the optimum temperature giving optimal mass conversion and minimum biodiesel viscosity.

3.3.2.3. Type and quantity of alcohol. Usage of both methanol and ethanol had been reported as the possible alcohol types for the trans-esterification of SHAFs and PFs using HAC route of synthesis. A high methanol to fat ratio of 30:1 was used for H_2SO_4 catalyzed transesterification of CF and MF resulting high biodiesel yields [17]. Tashtoush et al. [96] used both methanol and ethanol for transesterification of SHAF at three levels of excess ethanol viz. 100, 150 and 200% of SHAF. The mass conversion to biodiesel decreased on increasing the excess alcohol concentration beyond 100% possibly due to decrease in catalyst concentration in reaction mass at higher levels of excess alcohol. In producing biodiesel from BT, Encinar et al. [71] probed into the effect of methanol to fat ratio on biodiesel yield employing three levels of 6:1, 12:1 and 18:1. Interestingly, methanol to fat ratio of 6:1 gave highest yield during the initial phase of reaction, nonetheless, after 48 h reaction duration, the yield for all the three MRs were found same under otherwise identical conditions; indicating attainment of reaction equilibrium. Thus, the alcohol concentration should be optimized to obtain highest biodiesel yield for a given process conditions

3.4. Heterogeneous catalytic transesterification

Heterogeneous catalysts offer number of advantages viz. easy product separation and purification, catalyst reusability, decreased acid or basic waste stream generation resulting in less environmental impact and improved overall process economy in comparison with their homogeneous counterpart [50]. The literature published works in the field of both acid and base heterogeneous catalytic

transesterification of fat extracted from different resources of SHAFs and PFs are critically reviewed in the following sections.

3.4.1. Heterogeneous acid catalysts

Soldi et al. [97] used a novel sulfonated polystyrene compound (SPS) as an acid heterogeneous catalyst possessing high concentration of active sites that rendered higher efficiency than other ion-exchange resins for the methanolysis of BT. SPS catalyst was used with varying methanol to BT ratio (from 3:1 to 100:1) at temperatures from 28 to 64 °C for transesterification of BT. Similarly, ethanolysis of BT was done using 20% of SPS catalyst with ethanol to BT ratio of 100:1 for 18 h at 64 °C, that led to a maximum BT conversion of 75%. The polymeric SPS catalyst could be recovered from the reaction mixture by sequential filtration, washing and drying to obtain the regenerated catalyst worthwhile for a new reaction cycle. In another work [98], Zr-SBA-15 was used as a highly efficient catalyst for the transesterification of PL and mixed fat (mixture of PL, BT and CF) and FAME yields of > 90% and 90% were obtained for respective feedstocks at a catalyst concentration of 12.45%. Catalyst reusability studies were performed by recalcination at 450 °C; and the catalytic efficacy was tested by transesterification of the said SHAFs and PF under reaction conditions of 209 °C, 45.80:1 methanol to fat ratio and 6 h of reaction time. The yield thus obtained was 90% for both PL and mixed fat, indicating satisfactory reusability attributes. Morales et al. [99] prepared arenesulfonic acid functionalized SBA-15 silica heterogeneous mesoporous acid catalyst and the catalytic activity was shown through transesterification of two categories of SHAF including PL and mixed fat (blend of CF, PL and BT). A maximum conversion of 85% has been reported under optimized conditions of 160 °C temperature, methanol to fat molar ratio of 30:1 and 8 wt% catalyst concentrations under constant stirring at 2000 rpm for 2 h.

It may, thus be observed that, although an appreciably high yield may be feasible; however, a higher catalyst concentration, reaction temperature, alcohol to SHAF ratio may be required while using heterogeneous acid catalysts in place of their homogeneous equivalents.

3.4.2. Heterogeneous base catalysts

Magnesium oxide impregnated with KOH was employed as a base heterogeneous catalyst (4 wt%) with methanol to fat ratio of 22:1 for transesterification of MF [100] and an optimized yield of > 98% was achieved at 65 °C in just 20 min. Liu et al. [101], produced biodiesel from PF using calcined Mg–Al hydrotalcite (CHT) catalyst. A fixed catalyst/total reaction volume of 0.04 g/mL at 120 °C with 60:1 methanol to PF ratio could result 98% fat conversion with 94% FAME content. The catalyst, however, underwent appreciable deactivation in the first reaction cycle owing to deactivation of the strongest base sites, although subsequent reaction cycles portrayed stable activity. Remarkably, the CHT demonstrated high surface basicity and high thermal stability enabling complete catalyst regeneration by recalcination in air. Calcium-manganese oxide (CaMnOx), calcium oxide (CaO), calcium iron oxide (CaFeOx), barium iron oxide (BaFeOx), barium manganese oxide (BaMnOx), calcium zirconium oxide (CaZrOx) and calcium cerium oxide (CaCeOx) [102] were employed as base heterogeneous catalysts for the transesterification of PL. All these catalysts showed a very high basicity ($\text{pH} > 11$), however, a significant catalytic activity was only displayed by CaMnOx , and CaO giving a product purity (wt%) of 98.0% and 94.6% respectively at 5 wt% catalyst concentration. The results also indicated that, higher catalyst concentration facilitated faster and higher conversion. Besides, catalyst reusability studies of CaMnOx depicted promising results.

3.5. Enzymatic process

Biodiesel production process catalyzed by enzymes could be more environmental friendly as compared to the conventional catalytic processes [103]. It was found that different lipases such as *Mucor miehei*, *Pseudomonas cepcia*, *C. Antarctica* and *Bacillus subtilis* were effective in transesterification of high FFA feedstocks [104–106]. However, product contamination caused due to the presence of residual enzyme and higher costs of the enzymes compared to chemical catalysts are the main drawbacks associated with enzyme-catalyzed reactions [107,108]. Nevertheless, unique specificity and effectiveness in minimizing undesirable side reactions are the main advantages of lipase-catalyzed process [109]. While studying several factors affecting biodiesel yield viz. temperature, water content, solvent, lipase and methanol concentrations employing immobilized *Candida sp.* 99-125, Lu et al. [110] observed that lipase-catalyzed transesterification (methanolysis) of PL was a time consuming process. The process involved

successive addition of 1/3rd equivalent of methanol to the system at 0 h, 10 h and 20 h that resulted 87.4% FAME yield at the end of 30 h. Repetitive usage of the immobilized lipase up to seven cycles provided more than 80% yield of biodiesel; however, further reuse of the immobilized lipase led to a substantial reduction in yield to a meager 34.7%. Zuhair et al. [36], studied the continuous SC-CO₂ process of biodiesel production from LM using immobilized lipase. The continuous process was conducted at an appreciably high pressure of 200 bar at temperatures of 45 °C and 60 °C for extraction and transesterification respectively. The used enzyme on washing with SC-CO₂ could retain its activity up to three successive runs; but the activity dropped to 27.3% in the next run. On the contrary, washing with t-butanol resulted in regaining of 91% activity of enzyme making it more effective washing solvent. Thus, enzyme catalyzed transesterification of SHAF could not provide high yield of biodiesel within shorter reaction time in spite of being much environmental friendly.

Table 4

An overview of few fuel properties of biodiesel derived from beef tallow.

Biodiesel	Cetane no.	Na (mg/kg)	Iodine no.	Cloud point (°C)	Pour point (°C)	Reference
BT100	60.35	1.63	–	–	–	[80]
BT100	–	–	35	–	–	CT [89]
BT100	–	–	35	–	–	UI [89]
BT100	–	2	44.4	–	–	WW R [31]
BT100	–	0.2	44.6	–	–	
BT100	–	–	–	12	– 2.2	[79] ^a
BT100	–	–	–	15	3	[75]
BT100	–	1.63 ± 0.52	41.5	–	–	[81]
BT100	57.8	–	–	14	12	[82] (biodiesel ethanol blend)
BT95	53.5	–	–	14	9	
BT80	50.3	–	–	11	6	
BT65	48.2	–	–	11	6	
BT55	45.0	–	–	9	6	
BT100	–	4.2	51.5	–	–	[77]

BT 100: BT biodiesel; BT “N”: Diesel blend with N% BT biodiesel; CT: Conventional transesterification; UI: Ultrasonic Irradiation; WW: Purification by water wash; R: Purification by Ion exchange.

^a BT 100 produced from 60:40 blend of sunflower oil to BT.

3.6. Supercritical methanol (SCM) trans/esterification process

There had been scanty work on the conversion of SHAF and PF using SCM process. For feedstocks such as SHAF and PF with high FFAs, both esterification of FFA and transesterification of triglycerides can take place simultaneously (in absence of any catalyst or enzyme) rendering higher yield without any pre-esterification process. SCM trans/esterification process uses methanol at very high temperature and pressure typically in the range of 350–400 °C and 45–65 MPa respectively [111]. Shin et al. [95] investigated SCM transesterification of refined PL which resulted maximum 89.91% FAME yield at 335 °C, 500 rpm agitation speed, 45:1 methanol to PL ratio, 20 MPa pressure over 15 min reaction duration. The researchers concluded that SCM method under such conditions were equally applicable even for waste lard samples containing higher amounts of FFA and water. Marulanda et al. [112] explored the SCM transesterification of CF that rendered maximum 88% biodiesel yield at 400 °C, 41.1 MPa, methanol/fat molar ratio of 6:1 in 5 min reaction duration. Interestingly, the authors pointed out that the process involved low alcohol excess for reaction and low byproduct glycerol formation owing to glycerol decomposition and consumption upon formation by methanol yielding glycerol ethers.

Table 5

An outline of beef tallow research analyzing properties of BT derived biodiesel.

Esters (%)	MeOH (%)	Water content (mg/kg)	LME (wt%)	glycerol total (%)	glycerol free (%)	Calorific value (KJ/Kg)	MG (%)	DG (%)	TG (%)	Reaction time	Conversion (%)	Reference
97	0.1	–	–	0.33	0.01	–	0.13	0.12	0.07	–	–	BT100 [80]
–	–	–	–	< 0.1	< 0.005	–	< 0.1	< 0.05	< 0.05	1 h	91	BTCT [89]
–	–	–	–	< 0.1	< 0.05	–	0.2	< 0.05	< 0.05	70 s	92	BTUI
–	–	374	0.63	–	–	–	–	–	–	2 h	90.8	BT100 (WW)
–	–	795	0.65	–	–	–	–	–	–	2 h	90.8	BT100(R) [31]
–	–	–	–	–	–	41,320	–	–	–	60 min	–	[79]
97.3	–	50	–	–	–	–	–	–	–	2 h	98.6	[71]
–	–	–	–	–	–	42,365	–	–	–	–	–	[75]
–	–	–	–	–	–	40.29	–	–	–	90 min	–	BT100 [82]
–	–	–	–	–	–	39.71	–	–	–	90 min	–	BT95
–	–	–	–	–	–	37.98	–	–	–	90 min	–	BT80
–	–	–	–	–	–	36.25	–	–	–	90 min	–	BT 65
–	–	–	–	–	–	35.01	–	–	–	90 min	–	BT 55
97.8	0.18	–	–	–	–	–	–	–	–	–	97.8	[77]

BT 100: BT biodiesel; BT “N”: Diesel blend with N% BT biodiesel; BTCT: BT biodiesel through Conventional transesterification; BTUI: BT biodiesel through Ultrasonic Irradiation; WW: Purification by water wash; R: Purification by Ion exchange; LME: Linolenic methyl ester; MG: Mono glyceride; DG: Di glyceride; TG: Tri glyceride.

3.7. Process intensification (PI) methods

process more robust and economically profitable [113]. PI techniques involving different kinds of advanced equipment viz. centrifugal contact separator (CCS), membrane reactor (MR), ultrasonic cavitation reactor (UCR) [113] for improved production of biodiesel from a wide spectrum of sources including high FFA feedstocks have been reviewed. UCR could provide greater than 99% biodiesel yield and also demonstrated excellent energy efficiency.

The novel ultrasonic irradiated transesterification of BT required only 70 s as compared to 1 h for conventional transesterification to achieve the same yield; the phenomena was ascribed to the high mass transfer rates due to formation of microemulsion through ultrasonic cavitation [89]. Radiofrequency (RF) aided transesterification of BT rendered $96.3 \pm 0.5\%$ biodiesel yield in a remarkably short 5 min reaction time [114]. Though, these reactors

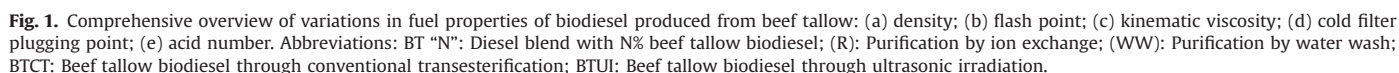


exhibit huge potential for biodiesel production, but further research will be required to overcome certain technical and process limitations [115].

The unique pyrolysis process [116] for BT conversion to biodiesel employed activated charcoal supported palladium catalyst in an electric furnace at 420 °C. The reaction pathways involved decomposition of TGs into fatty acids (FAs) and of unsaturated FA chains into HCs. Notably, the process did not use any alcohol and the biodiesel obtained possessed lower pseudo cold filter plugging point (CFPP) and higher calorific value compared to transesterified biodiesel. Very recently, Chakraborty and Sahu [117] demonstrated optimized application of infrared radiation for significant intensification of biodiesel production from waste goat tallow.

3.8. Properties of SHAF and PF derived biodiesel

3.8.1. Properties of biodiesel from BT

Taravus et al. [79] used sunflower oil and BT blend as feedstock and demonstrated that the water content in the resulting biodiesel is nearly six folds lower than biodiesel from 100% BT. Mata et al. [31] reported that for BT biodiesel, the resin (R) purification was more effective in reducing biodiesel acidity and kinematic viscosity (KV), whereas water washing (WW) followed by adsorbent drying and filtration provided better results concerning water, Na and K metal content. Interesting results were reported on the variations in biodiesel properties due to alterations in the blending proportions of biodiesel with commercial diesel and ethanol respectively.

Properties of biodiesel produced from BT have been elaborately presented in Tables 4 and 5. In the present article, a comprehensive and compact way of elucidating the important fuel properties of BT biodiesel has been devised using pictorial representation of the property values through radar plots (Fig. 1a–e).

Density [(kg/L), at 20 °C] of biodiesel should be kept as low as possible as it provides more blending options for improving the fuel quality without compromising performance. It can be observed (Fig. 1a) that the lowest reported density of pure “beef-tallow biodiesel” (i.e. BT 100) was 0.8305 kg/L [89]; which could be attributed to the intensified transesterification through ultrasonic irradiation. A 50% blend of biodiesel with conventional diesel [81] had higher density compared to 55%

Table 6
Fatty acid profile of biodiesel produced from different SHAFs.

Fatty acid	C no.	Beef tallow [81]	Mutton fat [17]	Pork lard [95]
Caprylic	C8:0	–	0.492	–
Capric	C10:0	–	0.370	–
Lauric	C12:0	–	4.385	–
Tridecnoic	C13:0	–	0.155	–
Myristic	C14:0	2.68	0.787	1.8
Myristoleic	C14:1	–	0.435	–
Pentadecanoic	C15:0	0.93	–	–
Palmitoleic	C16:1	1.90	0.422	2.5
Palmitic	C16:0	26.18	28.103	24.7
Heptadecanoic	C17:0	1.74	0.138	0.2
Linolenic	C18:3	–	–	1.5
Linoleic	C18:2	0.76	–	11.9
Oleic (cis isomer)	C18:1	30.09	31.279	44.9
Elaidic (trans isomer)	C18:1	1.74	–	–
Stearic	C18:0	33.69	27.195	12.1
Arachidic	C20:0	0.30	0.607	–
Ecosenoic	–	–	0.400	–
Behenic	C22:0	–	–	–
Eicosadienoic	C20:2	–	–	–
Eicosatetraenoic	C20:4	–	–	–
Eicosapentaenoic	C20:5	–	–	–
Docosapentaenoic	C22:5	–	–	–

Table 7
A complete overview of properties of biodiesel produced from pork lard.

Source	water (mg/kg)	density (kg/m ³)	Acid no. (mg KOH/g)	Kinematic viscosity (mm ² /s) at 40 °C	Methyl ester (wt%)	LME (wt%)	Iodine value (g _I /100 g)	Flash point (°C)	Cetane no.	Na (mg/kg)	Sulfur content (wt%)	Sulfated ash (wt%)	CFPP (°C)	Reference
WL	0.034%	872	0.01–0.03	4.64–7.73	69.6–99.6	1.4	77	–	–	–	–	–	–	[27]
RL	–	877	0.117	4.85	88.7	0.5	54.4	–	–	–	–	–	–	[87]
PF	< 0.005%	875–883	0.20	4.47	74.8–83.8	–	–	436	74.4	–	0.0002	< 0.005	–	[84]
Oil/lard mix.	–	–	0.02–0.10	4.46	93.9–96.6	1.0–5.3	67–127	174–179	–	–	–	–	–	[85]
Lard	–	–	0.08	4.2	–	–	72	–	–	–	–	–	8	[86]
PL	–	886	0.45	5.47	97.2	0.8	64.9	–	–	–	–	–	5	[77]
PL (WW)	–	873	0.22	5.084.84	–	–	75.6	147	–	17.2	–	–	4	[31]
PL (R)	–	871	0.17	–	–	–	77.3	147	–	62.1	–	–	5	[77]
PL	374.2	866	–	5.47	–	–	64.9	147	–	4.3	–	–	5	[119]
B20	–	873	0.55	3.15	–	–	75.6	147	–	–	–	–	–6	[119]

LME: Linolenic methyl ester; KV: Kinetic viscosity; CFPP: Cold filter plugging point; B “N”: Diesel blend with N% PL biodiesel; WL: Waste lard; PL: Pork lard; RL: Refined lard; PF: Pork fat; (R): Purification by ion exchange; (WW): Purification by water wash.

Table 8
Overview of biodiesel properties produced from fleshing oil.

Feedstock	H ₂ O (mg/kg)	density (kg/m ³)	Kinematic viscosity (at 40 °C)	Flash point (°C)	CFPP (°C)	Acid value (mg KOH/g)	Iodine value (gI/100 g)	Ester content (wt%)	Heat of combustion (KJ/kg)	Reference
RFO	180	876	4.2	175	–	0.21	56	97.23		[83]
FO	326.4	875.5	4.77	174.8	+ 11	0.32	61	95.5	39,954	[29]

RFO: Raw fleshing oil; FO: Fleshing oil.

Table 9
Outlines of properties of biodiesel derived from fleshing oil.

Feedstock	Free glycerine (wt%)	Total glycerine (wt%)	MeOH (wt%)	Mono- glyceride (wt%)	Di-glyceride (wt%)	Tri-glyceride (wt%)	Sulphated ash (wt%)	Copper corrosion test	Oxidation stability (110 °C h min)	Reference
RFO	0.019	0.16	–	0.31	0.045	0.194	0.001	1A	2.4	[83]
FO	0.01	0.10	0.01	0.27	0.09	0.04	–	No 1	–	[29]

RFO: Raw fleshing oil; FO: Fleshing oil.

Table 10
Summary of biodiesel properties derived from chicken and mutton fats.

Feedstock	Density Kg/L at 20 °C	Flash point (°C)	Kinematic viscosity (mm ² /s) at 40 °C	Water content (mg/kg)	CFPP (°C)	Cetane no.	Sulfur content (mg/kg)	AN (mg KOH/ g)	Iodine value (gI ₂ / 100 g)	Cloud point (°C)	Pour point (°C)	Reaction yield (wt%)	Ester content (wt%)	Na + K (mg/ kg)
CF [28]	0.869	74	2.8	127		48	23.45	–	–	–7	–			
CF (WW) [31]	0.877	171	6.86	1201	+3			0.55	78.8			76.8	73.80	46.8
CF (R) [31]	0.888	171	4.83	1273	+11			0.09	72.9			76.8	83.68	60.1
CF (B20) [31]			3.28		–8									23.9
CSF [78]	0.870	149.5	4.82		–2		8.1	0.07	77.77			83.5	97.7	0.67
CF [17]	0.867	–	7.20	100		61	–	0.251	130	–5	–6			
MF [17]	0.856		8.15	200		59		0.344	126	–4	–5			
CF [32]	0.891	172.8	4.94					0.22			2		88.5	

CF: Chicken fat; CSF: Chicken and swine fat mixture; (WW): Purification by water wash; (R): Purification by Ion exchange method; B “N”: Diesel blend with N% CF biodiesel; AN: Acid number; MF: Mutton fat.

Table 11
Fatty acid profiles of biodiesel produced from different PFs.

Fatty acid	C no.	CF [17]	DT [91]	FM [33]	Mixed PF [118]
Caprylic	C8:0	0.0144	–	–	–
Capric	C10:0	0.0285	–	–	–
Lauric	C12:0	0.7901	–	–	–
Tridecnoic	C13:0	0.2465	–	–	–
Myristic	C14:0	0.2286	0.8	–	–
Myristoleic	C14:1	0.0827	–	–	–
Pentadecanoic	C15:0	–	–	–	–
Palmitoleic	C16:1	6.9231	0.3	–	3.71
Palmitic	C16:0	24.654	24.2	28.86	21.82
Heptadecanoic	C17:0	0.1419	–	–	–
Linolenic	C18:3	0.3832	–	–	1.78
Linoleic	C18:2	12.5832	2.2	14.44	27.02
Oleic (cis isomer)	C18:1	45.1812	72.5	46.10	36.59
Elaidic (trans isomer)	C18:1	–	–	–	–
Stearic	C18:0	6.2515	–	10.06	7.61
Arachidic	C20:0	0.0992	–	–	–
Ecosenoic		0.5863	–	–	–
Behenic	C22:0	0.0952	–	–	–
Eicosadienoic	C20:2	–	–	–	–
Eicosatetraenoic	C20:4	–	–	–	–
Eicosapentaenoic	C20:5	–	–	–	–
Docosapentaenoic	C22:5	–	–	–	–
Docosahexaenoic	C22:6	–	–	–	–

CF: Chicken fat; DT: Duck tallow; FM: Feather meal; PF: Poultry fat.

blend of biodiesel with ethanol [82], showcasing the advantage of biodiesel–ethanol blend. It is also evident from BT biodiesel density radar plot [82] that the density gradually decreases with decrease in blending percentage of BT biodiesel. A high flash point (FP) for biodiesel is recommended so that even at considerably high temperatures it would not catch fire. Radar plot analyses of FP (Fig. 1b) show that the highest achievable FP for BT biodiesel was 172 °C [31] irrespective of the FAME purification method. The BT biodiesel synthesized via process intensified ultrasonic irradiation possessed the lowest FP (146 °C). In general, FP gradually increases with increase in BT biodiesel content in blended fuel.

As evident from Fig. 1c, lowest KV can be observed for conventional diesel and with increase in BT biodiesel content in the diesel–biodiesel blend; the KV steadily increases signifying a disadvantage of BT biodiesel. As low blends of BT biodiesel will simultaneously decrease both KV and FP, thus, it would be required to simultaneously optimize FP and KV to improve the overall performance index of the biodiesel. Notably, CFPP is another important parameter that needs to be reduced to ensure suitable low temperature performance of the diesel fuel. The compiled statistics of CFPP for BT biodiesel (Fig. 1d) elucidates that with decrease in BT biodiesel content in the blend, CFPP decreases. However, Teixeira et al. [31] reported a CFPP value of + 10 °C for a 100% BT biodiesel which is considerably lower than

Table 12

A comprehensive overview of fuel properties of biodiesel derived from poultry fat.

Source	Kinematic viscosity (mm ² /s) at 40 °C	Dynamic viscosity (MPa s)	CFPP (°C)	Acid no (mg/g)	Glycerol total (wt%)	Glycerol free (wt%)	Cloud point (°C)	Pour point (°C)	Yield (%)	Density (kg/m ³)	Flash point (°C)	Higher heating value (MJ/kg)	Reference
PF:B100	4.386		2	0.298	0.143	0.001	7	3					(PFMB) [118]
PF:B5	3.50	4.12	8				7	1					(PFEB) [92]
PF:B10	3.52	4.15	8				7	2					
PF:B15	3.54	4.21	8				7	2					
PF:B20	3.58	4.25	8				7	2					
PF:B50	4.16	4.68	7				6	−4					
PF:B100	4.75	5.65	7				6	−4					
PF:B5	3.62	4.10	4				5	−2					(PFMB) [92]
PF:B10	3.62	4.35	4				5	−2					
PF:B15	3.66	4.32	5				6	−2					
PF:B20	3.69	4.33	5				6	−1					
PF:B50	4.05	5.03	7				6	−2					
PF:B100	4.71	5.41	5				7	−1					
PF:B100	6.86		3	0.55					76.8	877	172	39.58	(PFMB) [119]
PF:B20	3.28		−8									44.71	

PF: B “N”: Diesel with N% PF biodiesel ; PFEB: Poultry fat ethyl biodiesel; PFMB: Poultry fat methyl biodiesel.

reported by any other work [80,89]. The research of Taravus et al. [79] revealed that a 60:40 blend of sunflower oil to BT as feedstock could reduce the CFPP of product biodiesel to a commendable -2°C . Nonetheless, as the BT ratio in the feed mixture increased, CFPP was found to increase gradually.

AN has a threshold of 0.3 as per biodiesel standard set by most of the industrial manufacturers. Fig. 1e elucidates that purification protocols such as water washing followed by adsorbent drying and filtration or ion exchange resin process [31] should be followed in order to make biodiesel conforming to market specification (AN below 0.3). Table 6 enumerates that BT and MF derived biodiesel possess large amount of saturated fatty acids (C16:0, palmitic; and C18:0, stearic) rendering high cetane number and exhibiting less propensity to oxidation and polymerization. Conversely, saturated fatty acids undergo crystallization at lower temperatures posing constraint to BT and MF biodiesel usage in cold climates.

Thus, it may be concluded that 100% BT biodiesel gives a favorable highest FP; however, other parameters viz. density, KV and CFPP are adversely affected due to increase in BT biodiesel content in a blended diesel fuel. Remarkably, blending of BT biodiesel with ethanol or diesel improves its fuel properties considerably.

3.8.2. Properties of biodiesel from PL

The fatty acid profile and properties of PL biodiesel are presented in Tables 6 and 7 respectively. It may be inferred that due to high concentrations of unsaturated linoleic and oleic acids, PL biodiesel has propensity to oxidation and polymerization. Dias et al. [27,85] elucidated the properties of biodiesel obtained from acid waste lard and oil-lard blend. It was observed that AN of the biodiesel for former [27] was lesser than the latter [85] at the cost of its higher KV. It is worthy to note that all the fuel properties of PL biodiesel were not in accordance with EN 14214 [85]. Nevertheless, Phalakornkule et al. [88] reported FP, cetane number and other important fuel properties conforming to Thai standards. As evident from Table 8, the lowest possible value of CFPP (i.e. -6°C) and KV (3.15 mm²/s) could be achieved by 20% blend of PL biodiesel with conventional diesel.

3.8.3. Properties of biodiesel from FO sourced from leather industry

The fuel properties of FO derived biodiesel have been presented in Tables 8 and 9. Alptekin et al. [29] compared his results with

both EN 14214 and ASTM-D6751-10 simultaneously. KV, AN, methanol content, mono-glyceride, di-glyceride, tri-glyceride, free glycerin, total glycerin, iodine value and copper corrosion were found out to be in accordance with the standards. Unfortunately, the sulfur content (141 mg/kg) was much higher and the ester content of 95.5 wt% was slightly lower than the allowable range. On the contrary, although methyl ester and sulfur content in FO biodiesel [83] were found acceptable; nonetheless, it could not meet EN 14214 specification for CFPP and oxidation stability.

3.8.4. Properties of biodiesel from chicken fat (CF)

Mata et al. [31] presented a comparative study between the properties of biodiesel derived from waste CF and that of commercial diesel fuel revealing the commercially viable properties of B10 blend of CF biodiesel (Table 10). Bhatti et al. [17] had demonstrated the superiority of CF as a better feedstock for biodiesel production than SHAF (viz. mutton fat). CF biodiesel exhibited higher cetane number, iodine value, AN and calorific values and lower pour point and cloud points than MF derived biodiesel as depicted in Table 10. Notably, the lowest CFPP and AN of 100% biodiesel was reported while utilizing chicken-swine fat mixture as the feedstock [78]. Fatty acid composition (Table 11) of CF biodiesel indicates high concentration of unsaturated fatty acids making it viable for oxidative degradation.

3.8.5. Properties of biodiesel from PF wastes (mixed)

Heterogeneous mixed PF, which contains fats derived from wide range of poultry animals with no consistent composition, had been employed in production of biodiesel by Tang et al. [118], Ramalho et al. [92] and Mata et al. [119] and the resultant properties are presented in Table 12. Mixed PF although has properties similar to cotton seed oil and soybean oil, nonetheless, the product biodiesel possesses inferior properties as compared to those of ultra-low sulfur diesel (ULSD). Ramalho et al. [92] reported the variations in PF methyl and ethyl biodiesel properties by altering blends with commercial diesel. It was revealed that B5 blend of ethylic biodiesel has a higher dynamic viscosity, CFPP, cloud and pour points than B5 blend of methylic biodiesel (Table 12) giving the latter an upper edge in low temperature performance of the fuel. Mata et al. [119] could demonstrate

a great reduction in KV and CFPP of PF biodiesel when blended (B20) with petroleum diesel. Presence of higher percentage of saturated fatty acids (Table 12) in PF biodiesel may result in increased value of cloud and pour point and KV [118].

4. Conclusion and future prospects

It has been evident that both SHAF and PF feedstocks can prove to be very potential feedstock for high quality biodiesel production owing to ease of availability and cost-effectiveness. Sulfuric acid has been most extensively used homogeneous acid catalyst for trans/esterification while both NaOH and KOH have been used as economical homogeneous base catalysts preferentially for trans-esterification of SHAFs and PFs. Two-step trans/esterification is usually applied to feedstocks with high AN; while single-step trans/esterification, is usually applied to SHAFs and PFs having low AN. Heterogeneous acid/base catalyzed trans/esterification of SHAF and PF employs relatively higher values of methanol/ethanol to fat molar ratio, reaction temperature and catalyst concentration in comparison with their homogeneous counterpart. Enzymatic trans/esterification process, although usually time-consuming; nevertheless, it offers advantage of processing of high AN feedstocks without chemical pre-treatment. Supercritical methanol process requires adverse high temperature and pressure conditions making it economically unfavorable.

Process intensification techniques have the capability to reduce the reaction time, temperature and pressure requirements by a remarkable margin that can render an overall energy-efficient and cost-effective protocol for biodiesel synthesis. It is very imperative for the SHAF and PF derived biodiesel to conform to the international standards. Though the biodiesel produced from SHAF and PF feedstocks has high favorable flash point; however, undesirable higher values of CFPP and KV compared to those of commercialized diesel are matters of great concern. Fortunately, appropriate blends of SHAF/ PF biodiesel with commercial diesel exhibited acceptable fuel properties.

Un-utilization of animal fats might craft appreciable aesthetic and upsetting health and environmental crisis. Owing to the technical feasibility of biodiesel production from SHAFs and PFs with inherently associated environmental and economical benefits, SHAFs and PFs should be judged as prospective feedstocks in biorefinery. Utilization of these cost-effective feedstocks coupled with execution of improved conversion technologies will definitely make biodiesel economically more viable besides solving waste disposal problem. Thus, these low-cost feedstocks should be employed in large and small biodiesel production plants for sustainable development which would certainly contribute to significant growth of country's GDP. This would also facilitate developing a low carbon economy to realize Governments' commitment to the Kyoto Protocol.

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